

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in or relating to the Oxy-chlorination of Hydrocarbons

We THE DISTILLERS COMPANY LIMITED, a British Company, of 12, Tophichen Street, Edinburgh 3, Scotland, do hereby declare the invention, for which we pray that a patent 5 may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to the oxychlorination 10 of aliphatic hydrocarbons and in particular to the oxychlorination of aliphatic hydrocarbons containing up to four carbon atoms per molecule.

The production of chlorinated hydrocarbons 15 by reaction of hydrocarbons with hydrogen chloride and oxygen in the vapour phase at elevated temperature in the presence, as catalyst, of cupric chloride deposited on a support is known.

It is an aim of the present invention to provide an improved catalyst for the oxychlorination of aliphatic hydrocarbons.

According to the present invention the process for the production of chlorinated hydrocarbons 20 comprises contacting a feed containing an aliphatic hydrocarbon having up to four carbon atoms per molecule, hydrogen chloride and molecular oxygen in the vapour phase at elevated temperature with a catalyst comprising combined copper, combined alkali metal and/or combined alkaline earth metal and combined zirconium, uranium, thorium and/or titanium deposited on activated alumina that has been subjected to a heat treatment in air in the temperature range 600 to 1,200° C., preferably 900 to 1200° C., for about 2 to 24 hours.

Under the reaction conditions the catalyst is thought to contain the combined metals at least partially in the form of the metal oxides, chloride or oxychlorides.

The catalyst as prepared for use in the process may suitably comprise compounds of copper such as copper oxide or copper chloride, which may be applied to the support in any suitable manner. For example, the support may be impregnated with a solution of copper chloride, dried and used as such in the reactor. Alternatively the support may be impregnated with a solution of a copper salt, e.g. the nitrate or formate, which is then converted into copper oxide within the pores of the support by either thermal decomposition or chemical hydrolysis suitably followed by drying. Where the catalyst is copper oxide formed by the thermal decomposition of a copper salt on a support the thermal decomposition to the oxide can take place during the oxychlorination reaction at the reaction temperature employed. The catalyst should preferably contain about 0.5 to 10% by weight of copper calculated as the metal.

The catalyst suitably contains about 0.2 to 10% by weight of alkali metal and/or alkaline earth metal. The combined alkali or alkaline earth metal may be incorporated with the catalyst in any suitable manner, for example by impregnation of the support before or after heat treatment if employed with a solution of a suitable salt or mixture of salts. The impregnation may be carried out before, after or simultaneously with the deposition of the copper compound. Suitable alkali or alkaline earth metal salts include

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- hydroxides, chlorides, aluminates and/or nitrates. Organic salts such as formates, oxalates and/or acetates may also be used. The catalyst may contain more than one alkali and/or alkaline earth metals. The preferred alkali metals are sodium and potassium. The preferred alkaline earth metal is magnesium.
- The catalyst suitably contains zirconium, uranium, thorium and/or titanium in proportion ranging from about 0.2 to 10% by weight calculated as the metal. It has been found that the incorporation of zirconium, uranium, thorium and/or titanium increases the activity of the catalyst, while greatly reducing the risk of loss of copper from the catalyst surface by volatilisation. The combined zirconium, uranium, thorium, and/or titanium may be incorporated with the catalyst in any suitable manner, for example by impregnation of the support before or after heat treatment with a solution of a suitable salt or mixture of salts. The impregnation may be carried out before, after or simultaneously with the incorporation of the copper, alkali metal and/or alkaline earth metal compounds. Suitable zirconium, uranium, thorium or titanium salts are for example hydroxides, chlorides or oxy-chlorides, carbonates, or nitrates including basic nitrates. Organic compounds such as formates, acetates, or oxalates may also be used. The use of the oxalate is particularly convenient. In addition, certain organometallic compounds such as butyl titanates, may be employed which may be decomposed to the corresponding metal oxide on the catalyst.
- As will be appreciated by those skilled in the art, there are numerous methods of preparing the catalyst, the present invention being in no way limited to one such particular method. As an alternative method of preparation to that described above there may be mentioned the addition of copper oxide or a compound that yields copper oxide when heated, an alkali metal and/or alkaline earth metal salt and a zirconium, uranium, thorium and/or titanium salt to an alumina hydrogel. In another method the copper, alkali and/or alkaline earth metal and zirconium, uranium, thorium and/or titanium metal compounds in powder form are mixed with the powdered support and the mixture formed into pellets.
- In carrying out the process the supported catalyst may be employed in a fixed bed in the form of pellets or granules or in a fluidised or moving bed.
- The hydrocarbon feed to the reaction may suitably comprise a paraffin and/or olefine having up to four carbon atoms per molecule. The preferred paraffin is ethane and the preferred olefine is ethylene. Ethane and ethylene may also be used in admixture together. The products are mainly 1,2-dichloroethane from ethylene and ethyl chloride, vinyl chloride, dichloroethanes and higher chloroethanes from ethane.
- The oxygen in the feed may be provided as pure oxygen or as an oxygen containing gas, e.g. air.
- The hydrogen chloride may be provided from any suitable source e.g. as waste hydrogen chloride from the pyrolysis of 1,2-dichloroethane to produce vinyl chloride. The hydrogen chloride may also be diluted or partially replaced by chlorine.
- While the reaction is not limited to particular ranges of feed composition it may be preferable to use hydrogen chloride and oxygen in a small stoichiometric excess over the hydrocarbon in order to obtain a high conversion of the latter. Thus for the oxychlorination of ethylene the gas fed to the reactor may, with advantage, contain 10—18 molar percent of ethylene together with hydrogen chloride and oxygen at concentrations corresponding to about 1.05 of the requirements of the following equation:
- $$\text{C}_2\text{H}_4 + 2\text{HCl} + \frac{1}{2}\text{O}_2 \rightarrow \text{C}_2\text{H}_4\text{Cl}_2 + \text{H}_2\text{O}$$
- The remainder of the gas mixture suitably consists of an inert diluent such as nitrogen. When the ethylene concentration is at or close to 18 molar percent the rest of the feed mixture is conveniently made up of air and hydrogen chloride without additional diluent.
- Reaction temperatures may suitably range from 200° to 500° C. The contact time may range from 1/10th to 30 seconds and is preferably about 0.5 to 15 seconds.
- The reaction may be carried out at pressures of from 1 to 10 atmospheres absolute. The use of super-atmospheric pressures is advantageous because the substantial part of the chlorinated product can be recovered by cooling to ambient temperature.
- The invention is illustrated further by the following examples in which parts by weight and parts by volume bear the same relationship as do grammes to millilitres.
- EXAMPLE 1**
- 42 parts by weight of 1/8" diameter pellets of a commercial alumina which had previously been heated for 24 hours at 1060° C. was impregnated with an aqueous solution containing 4.96 parts by weight of cupric chloride dihydrate, 0.972 parts by weight of potassium chloride and 3.9 parts by weight of uranium nitrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6(\text{H}_2\text{O})$). The mixture was evaporated to dryness and further heated until the nitrate had decomposed.
- It then contained 4% copper, 4% uranium and 1.1% potassium by weight.
- 2,457 parts by vol/hr. ethylene, 4,660 parts by vol/hr. hydrogen chloride and 5,900 parts by volume/hr. air were mixed and passed over 36 parts by volume of the catalyst, maintained at 325° C. in a fixed bed isothermal reactor.

The maximum conversion of hydrogen chloride to chlorinated products was 95.7% and only 0.6% of the ethylene was burnt to carbon dioxide.

EXAMPLE 2

- A catalyst was prepared by adding 80 parts by weight of a commercial activated alumina (in the form of 1/8" diameter pellets) which had been previously heated at 1060° C. for 24 hours to a solution of 5.4 parts by weight of cupric chloride dihydrate, 4.9 parts by weight of technical zirconium nitrate and 1.2 parts by weight of potassium chloride. The solution was evaporated to dryness with constant stirring and the resulting catalyst was heated at 400° C. for 3 hours in order to decompose the zirconium nitrate to give zirconium oxide.
- Ethylene 1,910 parts by vol/hr, air 4,250 parts by vol/hr. and hydrogen chloride 3,450 parts by vol/hr. were mixed and passed through the catalyst, 36 parts by volume in a fixed bed isothermal reactor at 300° C. The conversion of hydrogen chloride to chlorinated product was 99%.

EXAMPLE 3

- A catalyst was prepared by adding 84 parts by weight of a commercial activated alumina (1/8" diameter pellets), which had been previously heated at 1060° C for 24 hours, to a solution of 9.92 parts by weight of cupric chloride dihydrate, 13.75 parts by weight of technical grade zirconium nitrate and 2.58 parts by weight of sodium chloride in 100 parts by weight of water. The mixture was evaporated to dryness with constant stirring and then heated to decompose the zirconium nitrate to the oxide. The resulting catalyst contained 4% of copper, 4% of zirconium and 1.1% by weight of sodium.

Ethylene 1,900 parts by vol/hr, hydrogen chloride 3,630 parts by vol/hr. and air 4,550 parts by vol/hr. were mixed and passed over the catalyst 28 parts by volume, maintained at 290° in a fixed bed isothermal reactor.

The maximum conversion of hydrogen chloride to products was 99.5% and only 0.8% of the ethylene was burnt.

EXAMPLE 4

- 50 A catalyst was prepared exactly as described in Examples 1 and 2 except that instead of the alkali metal, a magnesium salt was used. The catalyst contained 4% of copper, 4% of zirconium and 1.1% by weight of magnesium.

Ethylene 2,450 parts by vol/hr, hydrogen chloride 4,660 parts by vol/hr. and air 5,850 parts by vol/hr. were mixed and passed over the catalyst, 36 parts by volume, maintained at 290° in a fixed bed isothermal reactor.

The maximum conversion of hydrogen chloride to products was 99.1% and only 0.6% of the ethylene was burnt.

EXAMPLE 5

A number of catalysts were prepared by adding 100 parts by weight of the support (commercial activated alumina, 9—18 mesh BSS test sieve, previously heated at 1050° C. for 24 hours) to a solution of 5.37 parts by weight of cupric chloride, 2.294 parts by weight of potassium chloride and 10.14 parts by weight of thorium nitrate hexahydrate in 100 parts by weight of water. The mixture was evaporated to dryness with constant stirring and dried for 6 hours at 120° C. after which it contained 2% copper, 1.2% potassium and 4% thorium.

EXAMPLE 6

Ethylene (2,420 parts by volume/hour) hydrogen chloride (4,610 parts by volume/hour) and air (5,930 parts by volume/hour) were mixed and passed over 36 parts by volume of the catalyst supported on alumina prepared according to Example 5 above and maintained at 275° C. in a fixed bed isothermal reactor. The maximum conversion of hydrogen chloride to chlorinated products was 98.2%. Only 0.7% of the ethylene fed was burned.

EXAMPLE 7

5.36 parts by weight of cupric chloride dihydrate, 4.6 parts by weight of magnesium chloride hexahydrate, and 5.05 parts by weight of thorium nitrate hexahydrate were dissolved in the minimum amount of water and used to impregnate 42 parts by weight of 1/8th inch diameter pellets of commercial activated alumina which had previously been at 1060° C. for 24 hours. The mixture was evaporated to dryness with constant stirring and further heated to decompose the thorium nitrate to the oxide. The catalyst then contained 4% copper, 1.1% magnesium and 4% thorium.

1,943 parts by volume/hr. of ethylene, 3,652 parts by volume/hr. and 4,652 parts by volume/hr. of air were mixed and passed over 28 parts by volume of the catalyst at 300° C. in a fixed bed isothermal reactor. A maximum conversion of 93.6% of hydrogen chloride fed to chlorinated products was obtained and 1.7% of the ethylene formed carbon dioxide.

EXAMPLE 8

A catalyst was prepared by adding 95 parts by weight of commercial Actal* alumina, 1/8", pellets, which had previously been heat-treated at 1060° C for 24 hours to an aqueous solution of approximately 5.68 parts by weight of titanic oxalate dissolved in oxalic acid. Titanic oxalate was prepared by dissolving 8 parts by weight of titanic chloride in a concentrated aqueous solution of oxalic acid with heating. The mixture was evaporated to dryness with constant stirring, and heated for 1 hour at 400° C. to decompose the oxalate to the oxide. This mixture was allowed to cool, and was then added to a solution of 5.37 parts

- by weight of cupric chloride dihydrate and 1.14 parts of potassium chloride in 100 parts by weight of water. The mixture was evaporated to dryness with constant stirring and dried for 6 hours at 120° C, after which it contained 2% of copper, 0.6% of potassium and approximately 2% of titanium.
- 3,260 parts by volume/hours of ethylene, 6,220 parts by volume/hour of hydrogen chloride and 7,800 parts by volume/hour of air were mixed and passed through the catalyst, 40 parts by volume, maintained at 275° C. in a thermostatically controlled reactor.
- The maximum conversion of hydrogen chloride to chlorinated product was 96.5%. 1.7% of the ethylene fed was burnt to carbon dioxide.
- EXAMPLE 9
- A catalyst was prepared by impregnating 100 parts by weight of commercial Actal alumina (1/8" diameter pellets), which had previously been heated for 22 hours at 1060° C, with a 10% nitric acid solution containing 18.3 g. of zirconium nitrate, 11.9 g. of cupric chloride dihydrate and 22.3 g. of magnesium chloride hexahydrate. The resulting mixture was evaporated to dryness with constant stirring, dried for 6 hours at 110° C and finally heated at 400° C for 2 hours to decompose the nitrates, after which the catalyst contained 4% of copper, 4% of zirconium and 2.5% of magnesium.
- Ethylene (2,265 parts by volume/hr.), hydrogen chloride (4,755 parts by volume/hr.) and air (5,940 parts by volume/hr.) were mixed and passed through the catalyst (36 parts by volume) in a thermostatically controlled 1/4" diameter fixed bed reactor at 290° C. The conversion of hydrogen chloride was 95.1%, and 0.6% of the ethylene was burnt to carbon dioxide. The utilisation of ethylene was 100%.
- WHAT WE CLAIM IS:—
1. A process for the production of chlorinated hydrocarbons which comprises contacting a feed containing an aliphatic hydrocarbon having up to four carbon atoms per molecule, hydrogen chloride and molecular oxygen in the vapour phase at elevated temperature with a catalyst comprising combined copper, combined alkali metal and/or combined alkaline earth metal and combined zirconium, uranium, thorium, and/or titanium deposited on activated alumina which has been subjected to a heat treatment in air in the temperature range 600° to 1200° C for about 2 to 24 hours.
 2. A process as claimed in Claim 1 wherein the catalyst comprises copper chloride.
 3. A process as claimed in Claims 1 or 2 wherein the catalyst comprises copper oxide.
 4. A process as claimed in Claim 3 wherein the catalyst comprises copper oxide formed by impregnation of the alumina support with a solution of a copper salt and conversion of the deposited copper salt to copper oxide within the pores of the alumina by thermal decomposition or chemical hydrolysis.
 5. A process as claimed in Claim 4 wherein the copper salt is copper nitrate or copper formate.
 6. A process as claimed in Claims 4 or 5 wherein conversion to copper oxide is effected by thermal decomposition simultaneously with the oxychlorination reaction under the reaction conditions employed.
 7. A process as claimed in any of the preceding claims wherein the catalyst contains about 0.5 to 10% by weight of copper calculated as the metal.
 8. A process as claimed in any of the preceding claims wherein the catalyst contains about 0.2 to 10% by weight of alkali and/or alkaline earth metal.
 9. A process as claimed in any of the preceding claims wherein the combined alkali and/or alkaline earth metal is incorporated in the catalyst by impregnation of the alumina support with a solution of an alkali and/or alkaline earth metal salt before, after or simultaneously with the incorporation of the copper.
 10. A process as claimed in Claim 9 wherein the alkali and/or alkaline earth metal salt comprises a hydroxide, chloride, aluminate, nitrate, formate, oxalate or acetate.
 11. A process as claimed in any of the preceding claims wherein the alkali metal is sodium or potassium.
 12. A process as claimed in any of claims 1 to 10 wherein the alkaline earth metal is magnesium.
 13. A process as claimed in any of the preceding claims wherein the catalyst contains about 0.2 to 10% by weight of zirconium, uranium thorium, and/or titanium calculated as the metal.
 14. A process as claimed in any of the preceding claims wherein the combined zirconium, uranium, thorium and/or titanium is incorporated in the catalyst by impregnation of the alumina support with a solution of a zirconium, uranium, thorium and/or titanium salt before, after or simultaneously with the incorporation of copper, alkali metal, or alkaline earth metal.
 15. A process as claimed in Claim 14 wherein the zirconium, uranium, thorium and/or titanium salt comprises a hydroxide, chloride, oxychloride, carbonate, nitrate, oxalate, formate or acetate.
 16. A process as claimed in any of the preceding claims wherein the aliphatic hydrocarbon comprises a paraffin.
 17. A process as claimed in Claim 16 wherein the paraffin is ethane.
 18. A process as claimed in any of the preceding claims 1 to 15 wherein the aliphatic hydrocarbon comprises an olefine.

19. A process as claimed in Claim 18 wherein the olefine is ethylene.
20. A process as claimed in any of the preceding claims wherein the hydrogen chloride is waste hydrogen chloride from the pyrolysis of 1,2-dichloroethane to produce vinyl chloride.
- 5 21. A process as claimed in any of the preceding claims wherein the hydrogen chloride is diluted or partially replaced by chlorine.
- 10 22. A process as claimed in any of the preceding claims carried out at temperatures in the range 200° to 500° C.
- 15 23. A process as claimed in any of the preceding claims carried out at a contact time of 0.1 to 30 seconds.
24. A process as claimed in any of the preceding claims carried out at pressures of from 1 to 10 atmospheres absolute.
25. A process for the production of chlorinated hydrocarbons substantially as hereinbefore described with reference to the examples 1 to 4 & 6 to 10.
26. Dichloroethanes whenever produced from ethylene by a process as claimed in Claim 18.
27. Vinyl chloride whenever produced from ethane by a process as claimed in Claim 17.
28. Ethyl chloride whenever produced by a process as claimed in claim 17.

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